k = Boltzmann's constant
T = absolute temperature
N = Avogadro's number
V = atomic volume
η = shear viscosity
M = molecular weight
R = gas constant = Nk
ρ = density
y = reduced density = $b/4V$
b = molecular covolume = $\frac{16}{3}\pi N\sigma^3$

Subscripts

m = melting point
c = critical

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Manuscript received June 22, 1972; revision received July 14, 1972; paper accepted July 17, 1972.

A Note on the Equilibrium Partial Pressures of Vapors Above Sulfuric Acid Solutions

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The equilibrium partial pressures of sulfuric acid, sulfur trioxide, and water above aqueous solutions of sulfuric acid are of interest in several areas of chemical engineering. Applications for this information are found in the sulfuric acid industry itself, in industries which use sulfuric acid, and in the fuel industry where the dew point of sulfur-containing flue gases may be determined by the above described equilibrium. There are essentially two methods of obtaining this needed information, that is, the partial pressures can be directly measured or they can be calculated from other measurements using the principles of thermodynamics. This note points out some of the difficulties of calculating this equilibrium from other thermodynamic data and compares these calculated predictions with the available experimental data on vapor pressures.

THEORETICAL CONSIDERATIONS

Abel (1946) and Gmitro and Vermeulen (1964) have made the only published attempts to estimate the partial pressures of sulfuric acid, sulfur trioxide, and water above aqueous solutions of sulfuric acid. Abel based his estimates of the partial pressures of sulfuric acid and water upon the pure component enthalpy and entropy change during vaporization as well as liquid activity data and extrapolation of the reaction equilibrium data of Bodenstein and Katayama (1909) from 325°C down to 25°C. At the time that Gmitro and Vermeulen made their estimates, similar pure component data and the more detailed liquid-and- gas-phase data of Giauque (1960) and Giguere (1963), respectively, were available.

In general, the partial pressures of sulfuric acid and water are estimated from an equation of the following form:

$$\ln p_i = A_i(x, T) \qquad (1)$$

In this equation, i represents either water or sulfuric acid and A_i is a function of liquid concentration and temperature. Normally, this function is written in the following form:

$$A_i(x, T) = a_i + b_i \ln(T) + c_i(1/T) + d_iT + e_iT^2 \qquad (2)$$

In certain cases, as indicated by Abel and by Gmitro and Vermeulen, some of the coefficients of the right-hand side of this equation are zero. These coefficients are calculated from the available thermodynamic data and tabulated as functions of the liquid-phase composition in these articles.

The major difficulty involved in using formulas such as Equation (1) for the prediction of vapor pressures is the large mean uncertainty that can result in the predicted partial pressures from relatively small errors in the measured thermodynamic quantities. Part of the problem is illustrated by taking the derivative of Equation (1).

$$\frac{dp_i}{p_i} = dA_i \qquad (3)$$

This equation states that the fractional error in the predicted pressure is equal to the absolute error of the right-hand side of the predictive equation. For example, if one is dealing with low partial pressures such as the H_2SO_4 partial pressure, and we have a value of A_i of -10 with an error of 1, the fractional error in the predicted pressure p_i would be 1.0. Stated in another way, a 10% error in A_i results in a 100% error in p_i. This error multiplication factor can be seen if Equation (3) is rearranged as below.

$$\frac{dp_i}{p_i} = A_i \left(\frac{dA}{A_i}\right) \qquad (4)$$

Thus the % error of A_i is multiplied by A_i to determine the % error of p_i.

For the particular case of the partial pressures of water and sulfuric acid above aqueous sulfuric acid solutions, the equations of the form shown in Equation (2) can be rearranged such that each of the measured thermodynamic quantities used in the prediction are multiplied by a known coefficient which is an exact function of temperature. From this rearranged functionality, the effect of errors in the thermodynamic quantities upon the absolute error of the quantity A_i can be ascertained, and hence the percentage error in the partial pressure determined. For the concrete case of the partial pressure of the sulfuric acid as performed by Gmitro and Vermeulen, Equation (2) yields the following:

$$\begin{aligned} RA_i = {} & a\left[\frac{298}{T} - \ln\frac{298}{T} - 1\right] \\ & + b\left[\frac{298^2}{2T} - 298 + \frac{T}{2}\right] + c\left[\frac{298^3}{3T} - \frac{298^2}{2} + \frac{T^2}{6}\right] \\ & + \alpha\left[\frac{298^2}{2T} - 298\ln\left(\frac{298}{T}\right) - \frac{T}{2}\right] \\ & + \overline{C}_{p298}\left[\ln\left(\frac{298}{T}\right) - \frac{298}{T} + 1\right] + S^0(g) - S^0(l) \\ & + \frac{(\overline{F} - F^0)_{298}}{298} - H^0(g)\left(\frac{1}{T}\right) + H^0(l)\left(\frac{1}{T}\right) \\ & + \overline{L}_{298}\left[\frac{1}{T} - \frac{1}{298}\right] \end{aligned} \qquad (5)$$

From comparison of the predictions of this formula with experimental data, considerable error is expected in the temperature range near 398°K. Evaluation of the temperature-dependent terms, for example, terms such as $[298/T - \ln(298/T) - 1]$, etc., indicates that the heat capacity data have a small effect upon the accuracy of the prediction. However, small errors in the values of enthalpy and entropy of the pure component in the liquid and vapor phases greatly affect the value of A_i. For example, the value of the enthalpy of liquid sulfuric acid, $H^0(l)$, that is, the standard heat of formation of H_2SO_4 (l) at 298.15°K, used by Gmitro and Vermeulen (1964) was -193.91 kcal/mole. Wagman et al. (1968) recommend a value of -194.548. If the more recent value is taken as correct, the small error of 0.638 kcal/mole introduces an 81% error in the predicted partial pressure of H_2SO_4 at 398°K. There are similar errors associated with the enthalpy of the pure gas and the entropy of the gas and liquid. Thus the expected errors in the predicted vapor pressures of the sulfuric acid could be in the range of several hundred %. This is in contrast to the estimated mean uncertainty of 10 to 20% as given by Gmitro and Vermeulen. Similar difficulties are also inherent in the computations of Abel for the partial pressure of sulfuric acid. For the calculation of the partial pressure of the water over aqueous sulfuric acid better predictions would be expected since the pure component enthalpies and entropies are known to a somewhat greater accuracy. It should be noted that the above mentioned errors in the enthalpies and entropies of sulfuric acid implies that considerable error (as high as 10%) exists in the enthalpy and entropy changes of vaporization.

EXPERIMENTAL COMPARISONS

Greenewalt (1925) summarized the experimental data for the total pressure over sulfuric acid solutions taken prior to his paper and presented the results as

$$\log p = a_i + c_i/T \qquad (6)$$

He estimated that values obtained from these equations are accurate to ± 2% from 0°C to the boiling point for acid compositions from 10 to 95 wt. % H_2SO_4. The most recent experimental measurements appear to be those of Haase and Rehse (1959) and Haase and Borgmann (1963), which cover a wide range of temperature (58 to 315°C) and acid concentrations (44.4-97.5 wt. % H_2SO_4). Hornung and Giauque (1955) have determined highly accurate values for 57.6, 64.5, and 73.1 weight % acid but only over a 23 to 71.8°C range. Although this information is useful for some applications, the important calculation of the dew point of a sulfuric acid-water vapor mixture (for example, flue gas) requires further experimental knowledge of the composition of the vapor phase above the sulfuric acid solutions. Thus, for a full experimental determination of the thermodynamic condition of the vapor above sulfuric acid solutions the partial pressures of all vapor components must be measured or equivalently the total pressure and the vapor composition must be measured.

Experimental determinations of the vapor pressure of water above these solutions (equivalent to total pressure for liquid compositions below 85% acid) as taken by various authors appear to be in reasonable agreement, and these measurements also correspond to the theoretical predictions of Abel and Gmitro and Vermeulen. Experimentally Luchinski (1956) reports somewhat higher total pressures for given conditions than the other authors. Theoretically, one would not expect the above mentioned errors to exist in the water partial pressure predictions because the pure component enthalpies and entropies are known accurately. Uncertainties in the enthalpy and entropy changes of the vaporization of water are not of the order of several percent. Figure 1 shows theoretical and experimental comparisons of the partial pressure of water above sulfuric acid solutions.

On the other hand, experimental measurements of the partial pressure of the sulfuric acid above aqueous sulfuric acid solutions are more difficult to perform and hence are less prevalent. To date there have been three such measurements; Luchinski measured the sulfuric acid partial pressure from 85 to 100% sulfuric acid liquid composition. Haase and Rehse (1959) determined this partial pressure for the liquid composition range 44 to 97% sulfuric acid, and finally Haase and Borgmann (1963) point out errors in the previous Haase and Rehse work (1959) and performed partial pressure measurements in the range 64 to 79% sulfuric acid. Assuming that the second measurements were correct, the errors of the first measurements for 74% acid concentration were as large as 30% with an average error of 7%. The theoretical predictions and the experimental measurements of sulfuric acid vapor pressure as a function of temperature for various liquid phase compositions are plotted in Figure 2.

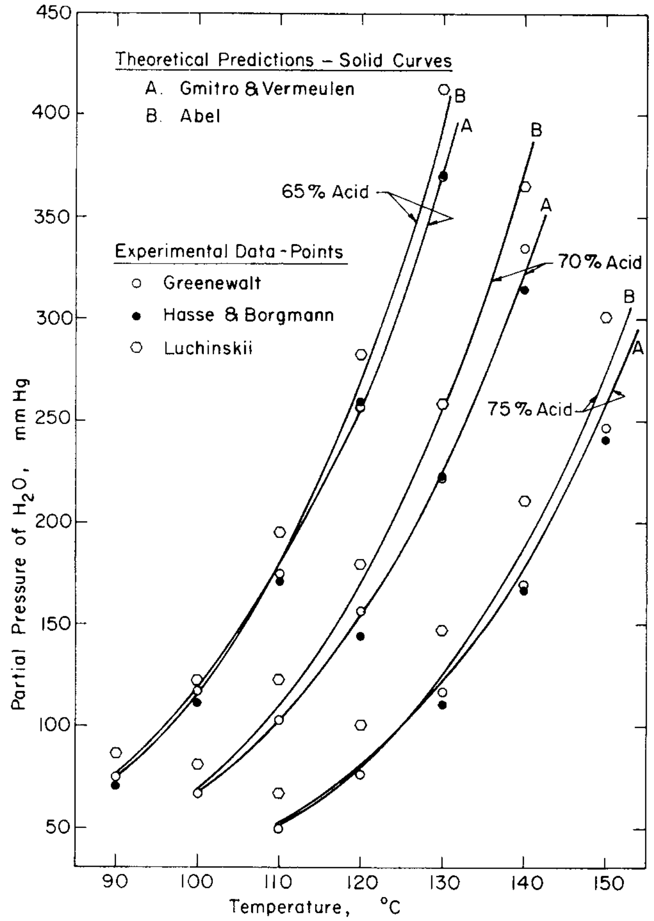

Fig. 1. Experimental measurements and theoretical predictions of water partial pressure above aqueous sulfuric acid solutions.

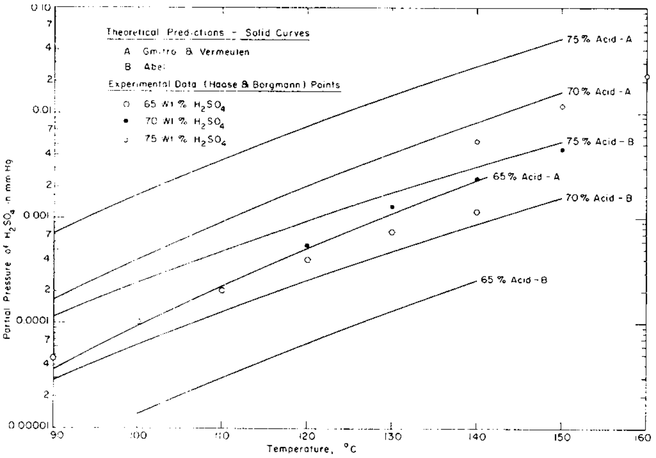

Fig. 2. Experimental measurements and theoretical predictions of sulfuric acid partial pressures above aqueous sulfuric acid solutions.

DISCUSSION AND CONCLUSIONS

Figure 1 indicates that the theoretical predictions of water vapor pressure correspond closely to that measured by experiment. The fact that the data of Luchinskii (1956) differ significantly sheds doubt upon his experimental technique. The comparison of theoretical predictions with experimental data for the partial pressure of sulfuric acid as shown in Figure 2 demonstrates that the predictions contain considerable error. This error apparently results from small uncertainties in the thermodynamic properties used in the prediction. From the present analysis, it is concluded that the best method to determine the vapor pressure of sulfuric acid above sulfuric acid solutions is to use the vapor pressure data of Haase and Borgmann (1963). The vapor pressure of water can be estimated by any of the previously discussed techniques.

In the prediction of flue gas dew points, it appears that data taken by Lisle and Sensabaugh (1965) again follow the data of Haase and Borgmann (1963). Dew point predictions based upon the work of Abel (1946) as has been done by Muller (1959) or based upon the work of Gmitro and Vermeulen (1964) as has been done by Snowden and Ryan (1969) do not appear to be reliable. Interestingly, Snowden and Ryan suggest that the reason dew point data do not fit their calculated predictions results from an adsorption phenomena.

In conclusion then it is apparent that for both sulfuric acid vapor pressure prediction and dew point prediction, one should use the experimental data of Haase and Borgmann (1963). Further, thermodynamic predictions of the vapor pressure of sulfuric acid above sulfuric acid solutions will remain tenuous until the necessary thermodynamic properties are defined more precisely.

NOTATION

a, b, c = pure component heat capacity coefficients
a_i, b_i, c_i, d_i, e_i = constants of correlation, Equation (2)
A_i = functionality for logarithm of partial pressure
$\overline{C}_{p298}$ = partial molal heat capacity at 298°K
F^0 = free energy at standard state
$\overline{F}$ = partial molal free energy
H^0 = pure component enthalpy at standard state
$\overline{L}$ = partial molal enthalpy
p_i = partial pressure
R = gas constant
S^0 = pure component entropy at standard state
T = temperature
x = weight fraction of sulfuric acid in solution
α = temperature coefficient of heat capacity

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Manuscript received July 18, 1972; revision received August 16, 1972; paper accepted August 18, 1972.

Dispersed Phase Reactor Model for Predicting Conversion and Mixing Effects

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A model recently developed by Zeitlin (1971) and Zeitlin and Tavlarides (1972a) combines a Monte Carlo technique, the concepts of drop or bubble coalescence and breakup in a turbulent flow field, and a description of the actual flow patterns and particle movements to describe agitated two phase dispersions. The model was applied by Zeitlin and Tavlarides (1972b, 1972c) to predict unsteady gas absorption with and without reaction and interphase transfer in extractors from limited amounts of data. An extension is presented here to study effects of macromixing and micromixing of the dispersed phase on conversion in a liquid-liquid system when the reactant diffuses from the dispersed to the continuous phase and zero, pseudo first- or second-order reaction occurs in the continuous phase. The cases of complete segregation, intermediate drop mixing (at various rev./min.), and pseudo complete drop mixing are compared.

Previous techniques to describe agitated dispersions were largely applied to systems in which the reaction takes place in the dispersed phase. Rietema (1958) calculated the ratio of residence times required to attain a given conversion for the two extremes of no mixing and complete mixing of the dispersed phase of a reactor for a zero-order reaction. Curl (1963) used a simplified population approach method assuming equal size drops with equal coalescence and breakage rates to study zero-order reaction in the dispersed phase of a well stirred flow reactor. Mingheng et al. (1966) employed a similar model in order to study effects of finite interdrop mixing on nonfirst-order reactions. Spielman and Levenspiel (1965) introduced a Monte Carlo technique to study the influence of coalescence on conversion for various reaction orders. Capovani and Tartarelli (1968) used a Monte Carlo technique to study conversion and selectivity for irreversible reactions in series as a function of zero and infinite coalescence rates. This model was modified by Tartarelli et al. (1970) to include two drop sizes and applied to study conversions for irreversible reactions.

Experimental investigations on interphase mass transfer with reaction in the continuous phase for liquid-liquid systems were made by Nagata and Yamaguchi (1960a, 1960b) and Nagata et al. (1960a). Effects of agitation intensity on resistance to mass transfer in the continuous and dispersed phases was studied. A simplified model was presented which could not accurately predict their experimental results at intermediate agitator speeds.

For systems similar to those discussed above, the distribution of concentration among the particle population depends upon circulation rates in the vessel, reaction or mass transfer conditions, rate and number of coalescences

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